

Magnetization Study of Cobalt Ferrite by Mean Field Approximation

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Abstract

The magnetic properties of cobalt ferrite (CoFe_2O_4) have been studied with the mean field approximation using the Bogoliubov inequality. An influence of temperature on the magnetization of cobalt ferrite was investigated in the absence and presence of crystal fields. The effect of exchange interactions revealed different behaviors of the magnetization versus the temperature; a pure ferrimagnetic state and a frustrated magnetic behavior were observed for the cobalt ferrite. In addition, the study of the exchange interactions effect on the total magnetization shows that for strong coupling interactions, the total magnetization of the system exhibits a jump at a given temperature. A first order phase transition from ferrimagnetic to ferromagnetic phase, a second order transition from ferromagnetic to paramagnetic phase and from ferrimagnetic to paramagnetic phase were observed.

Keywords: cobalt ferrite, mean field theory, ferrimagnetic

1 Introduction

The cobalt ferrite, CoFe_2O_4 , is of special interest because it has high cubic magnetocrystalline anisotropy and moderate saturation magnetization [1]. Furthermore, its good physical and chemical

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stability makes it a candidate for magnetoelectric transducer applications [2] and high-density magnetic storage applications such as high-density recording disks [3]. Cobalt ferrite, $\text{CoO} \cdot \text{Fe}_2\text{O}_3$, is magnetically hard, but all the other cubic ferrites are magnetically soft. The cobalt ferrite is ferrimagnetic with a Curie temperature of 789 K [4]. CoFe_2O_4 is an inverse spinel where the cations of 8Fe^{3+} occupy tetrahedral sites and 8Fe^{3+} occupy octahedral sites equally with 8Co^{2+} [5].

The magnetization of CoFe_2O_4 depends on a few factors: the cation distribution over tetrahedral and octahedral sites, the magnetic moment of each cation, the exchange interactions (J_{AA}, J_{BB}, J_{AB}), and the magnetization versus the temperature. The mean field (MF) approximation can be used to study the critical phenomena of bulk cobalt ferrite and the effect of different exchange integrals. The model of the MF approximation based on the Bogoliubov inequality has been used for different lattices systems [6-10]. The aim of this work is to study the magnetic properties of cobalt ferrite by the MF approximation depending on the cation distribution, the magnetic moment, the exchange interactions, and the crystal fields.

2 Method of Calculation

The Hamiltonian of the system is

$$H = -J_{AA}^{Fe-Fe} \sum_{ii'} S_i^{Fe} S_{i'}^{Fe} - J_{BB}^{Fe-Fe} \sum_{jj'} S_j^{Fe} S_{j'}^{Fe} - J_{BB}^{Fe-Co} \sum_{jj'} S_j^{Fe} S_{j'}^{Co} - J_{BB}^{Co-Co} \sum_{jj'} S_j^{Co} S_{j'}^{Co} - J_{AB}^{Fe-Fe} \sum_{ij} S_i^{Fe} S_j^{Fe} - J_{AB}^{Fe-Co} \sum_{ij} S_i^{Fe} S_j^{Co} - \Delta_{\text{Fe(tet)}} \sum_i (S_A^{Fe,Z})^2 - \Delta_{\text{Fe(oct)}} \sum_i (S_B^{Fe,Z})^2 - \Delta_{\text{Co}} \sum_i (S_B^{Co,Z})^2 \quad (1)$$

The sites of sublattice A are occupied by spins S_i^{Fe} , which take the values of $S_A^{Fe} = \pm \frac{5}{2}, \pm \frac{3}{2}, \pm \frac{1}{2}$, while sublattice B uses the values $S_B^{Fe} = \pm \frac{5}{2}, \pm \frac{3}{2}, \pm \frac{1}{2}$ and $S_B^{Co} = \pm \frac{3}{2}, \pm \frac{1}{2}$. The sums are over the nearest neighbors of the site, and the ion-to-ion exchange interactions between nearest neighbor atoms are given in Table 1 and Table 2. $\Delta_{\text{Fe}^{3+}(\text{tet})}$, $\Delta_{\text{Fe}^{3+}(\text{oct})}$ and $\Delta_{\text{Fe}^{2+}}$ are the crystal fields of each atom in each sublattice. The Hamiltonian used for the mean field calculations have been done in the absence of an applied magnetic field.

In order to treat the model approximately, the variational method based on the Bogoliubov inequality for the Gibbs free energy was employed [11], where $F(H)$ is the free energy of H given by Eq. (1). Therefore, the Gibbs-Bogoliubov inequality for the free energy per site of a system is

$$F \leq F_0 = -k_B T \ln(Z_0) + \langle H - H_0 \rangle_0 \quad (2)$$

The sublattice magnetizations per site m_I , m_{II} and m_{III} are defined as follows:

$$m_I = - \frac{\frac{5}{2} \exp\left(\frac{25\Delta_{\text{Fe(tet)}}}{4k_B T}\right) \sinh\left(\frac{5h_I}{2k_B T}\right) + \frac{3}{2} \exp\left(\frac{9\Delta_{\text{Fe(tet)}}}{4k_B T}\right) \sinh\left(\frac{3h_I}{2k_B T}\right) + \frac{1}{2} \exp\left(\frac{\Delta_{\text{Fe(tet)}}}{4k_B T}\right) \sinh\left(\frac{h_I}{2k_B T}\right)}{\exp\left(\frac{25\Delta_{\text{Fe(tet)}}}{4k_B T}\right) \cosh\left(\frac{5h_I}{2k_B T}\right) + \exp\left(\frac{9\Delta_{\text{Fe(tet)}}}{4k_B T}\right) \cosh\left(\frac{3h_I}{2k_B T}\right) + \exp\left(\frac{\Delta_{\text{Fe(tet)}}}{4k_B T}\right) \cosh\left(\frac{h_I}{2k_B T}\right)} \quad (3)$$

$$m_{II} = - \frac{\frac{5}{2} \exp\left(\frac{25\Delta_{\text{Fe(oct)}}}{4k_B T}\right) \sinh\left(\frac{5h_{II}}{2k_B T}\right) + \frac{3}{2} \exp\left(\frac{9\Delta_{\text{Fe(oct)}}}{4k_B T}\right) \sinh\left(\frac{3h_{II}}{2k_B T}\right) + \frac{1}{2} \exp\left(\frac{\Delta_{\text{Fe(oct)}}}{4k_B T}\right) \sinh\left(\frac{h_{II}}{2k_B T}\right)}{\exp\left(\frac{25\Delta_{\text{Fe(oct)}}}{4k_B T}\right) \cosh\left(\frac{5h_{II}}{2k_B T}\right) + \exp\left(\frac{9\Delta_{\text{Fe(oct)}}}{4k_B T}\right) \cosh\left(\frac{3h_{II}}{2k_B T}\right) + \exp\left(\frac{\Delta_{\text{Fe(oct)}}}{4k_B T}\right) \cosh\left(\frac{h_{II}}{2k_B T}\right)} \quad (4)$$

$$m_{III} = - \frac{3 \exp\left(\frac{9\Delta_{\text{Co}}}{4k_B T}\right) \sinh\left(\frac{3h_{III}}{2k_B T}\right) + \exp\left(\frac{\Delta_{\text{Co}}}{4k_B T}\right) \sinh\left(\frac{h_{III}}{2k_B T}\right)}{2 \exp\left(\frac{9\Delta_{\text{Co}}}{4k_B T}\right) \cosh\left(\frac{3h_{III}}{2k_B T}\right) + 2 \exp\left(\frac{\Delta_{\text{Co}}}{4k_B T}\right) \cosh\left(\frac{h_{III}}{2k_B T}\right)} \quad (5)$$

h_I , h_{II} , and h_{III} are the three effective fields. The orientation of the magnetic moments on the ground state are oriented down on tetrahedral sites $-5/2$ for Fe^{3+} , while magnetic moments of Fe^{3+} and Co^{2+} are oriented up on octahedral sites $+5/2$ for Fe^{3+} and $+3/2$ for Co^{2+} [12].

3 Results and Discussion

In the absence of crystal fields, Figure 1, the exchange constant between tetrahedral sites is positive and the partial magnetization in the tetrahedral site is negative corresponding to the spins of the tetrahedral sites to be ferromagnetically parallel. In the octahedral sites, the exchange constants are positive which leads the spins to be ferromagnetically parallel in the octahedral sites. The partial magnetization is positive for the cobalt and iron in the octahedral sites.

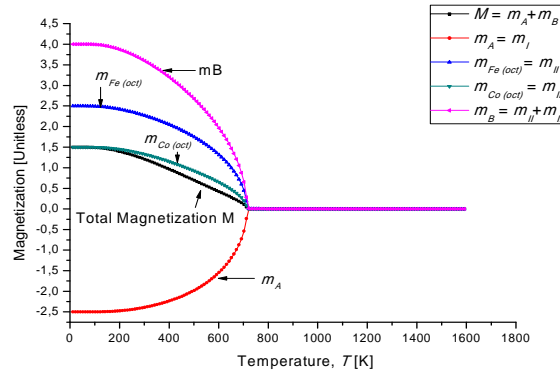


Figure 1: Magnetization versus temperature of CoFe_2O_4 with exchange interactions of Table 1

$J_{AA}^{\text{Fe-Fe}}$	$J_{AB}^{\text{Fe-Fe}}$	$J_{AB}^{\text{Fe-Co}}$	$J_{BB}^{\text{Fe-Co}}$	$J_{BB}^{\text{Fe-Fe}}$	$J_{BB}^{\text{Co-Co}}$
+14.0	-28.0	-22.7	+10.0	+9.0	+46.0

Table 1: Ion-to-ion exchange interactions J for CoFe_2O_4

The total magnetization or the order parameter is the difference between the partial magnetization of tetrahedral sites and the partial magnetization of octahedral sites. The order parameter is different than zero and decreases with increasing temperature below the critical temperature; the cobalt ferrite is acting as a pure ferromagnetic. At the Curie temperature of 722 K, the order parameter becomes zero accompanied with a broken symmetry, the magnetization versus temperature is continuous on the transition of second order. Above this critical temperature, the system loses its magnetization by being paramagnetic accompanied with a broken symmetry. Compared to the mean field Curie temperature, the Curie temperature of the magnetization curve in [13] is 793 K.

The variation of the exchange constant was studied with the magnetization constant versus the temperature by taking on consideration that the exchange constant are negative between tetrahedral sites and octahedral sites. It is remarked that the variation of the strength of the exchange interaction between the octahedral sites and tetrahedral sites lead to the increase of the Curie temperature (Figure 2).

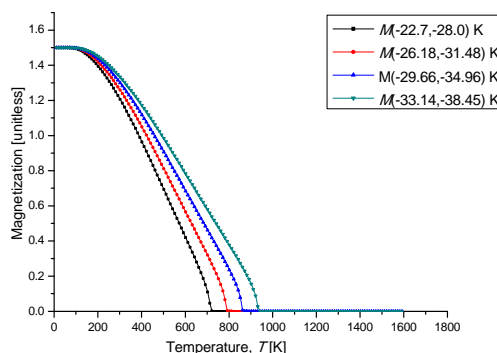


Figure 2: Effect of exchange interactions ($J_{AB}^{\text{Fe-Co}}$, $J_{AB}^{\text{Fe-Fe}}$) in the absence of crystal fields

In the presence of crystal field of cobalt in the octahedral sites, it is remarked that the order parameter of cobalt ferrite is continuous and decreases with increasing temperature until it vanishes at the Curie temperature of 800 K. There is a second transition from the ferrimagnetic state to the paramagnetic state, followed by a broken symmetry. It is also remarked that the Curie temperature for cobalt ferrites shifts from 700 K in Figure 1 to 800 K in Figure 3.

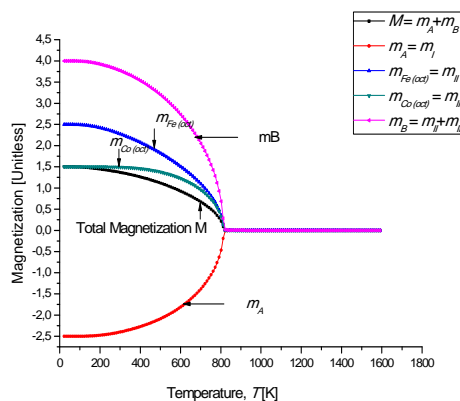


Figure 3: Magnetization versus temperature of CoFe_2O_4 with exchange interactions of Table 1 and crystal field of Co in the octahedral sites of 5802 K

In the presence of crystal field of Fe on the octahedral sites (Figure 4), there is a transition of second order from the ferrimagnetic state to the paramagnetic state, at the Curie temperature of 900 K, accompanied by broken symmetry. Below the critical temperature, the total magnetization is continuous.

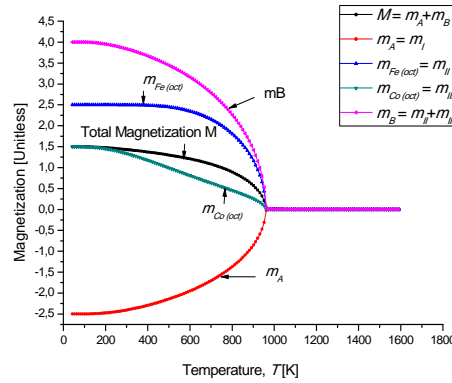


Figure 4: Magnetization versus temperature of CoFe_2O_4 with exchange interactions of Table 1 and crystal field of Fe on the octahedral site of 3481 K

In the presence of crystal field of Co and Fe in the octahedral and tetrahedral sites, the magnetization versus temperature is ferrimagnetic. Below the critical temperature, the order parameter is continuous and the partial magnetizations of the two sublattices are antiparallel. The magnetization is lost at the critical temperature of 1120 K (Figure 5), where it will be paramagnetic. The order parameter decreases with increasing temperature, and at the critical point, the order parameter becomes equal to zero and is accompanied with a broken symmetry.

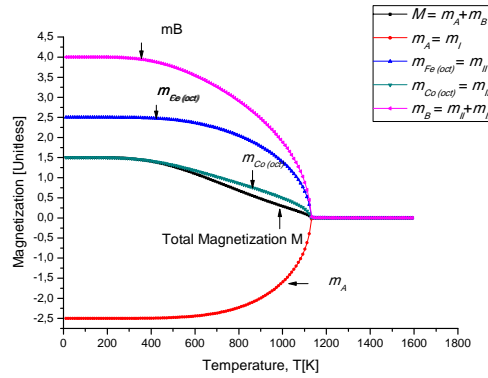


Figure 5: Magnetization versus temperature of CoFe_2O_4 with exchange interactions of Table 1 and crystal fields in tetrahedral sites of Fe and in the octahedral sites for Fe and Co, 348 K, 348 K and 348 K, respectively

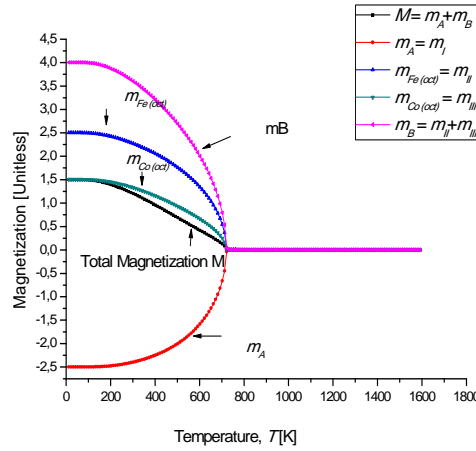


Figure 6: Magnetization versus temperature of CoFe_2O_4 with crystal field of iron in tetrahedral sites of 580 K

In the presence of crystal field of iron in the tetrahedral site, Figure 6, it is observed that the curve is acting ferrimagnetic until the Curie temperature of 700 K. There is a transition of second order from ferrimagnetic state to paramagnetic state.

In the absence of the crystal field in Figure 7, it is observed that the curve is acting as a ferrimagnetic state below the temperature of 350 K. The partial magnetization of the tetrahedral sites of iron and the octahedral sites of iron and cobalt are acting ferromagnetically antiparallel to each other and the order parameter is ferromagnetic at the temperature of 350 K. There is a magnetic frustration of the system, which has not been observed before for cobalt ferrite, caused by the different magnitudes and signs of the exchange constants in Table 2 [14], and the order parameter is discontinuous corresponding to a transition of first order. Above this transition, the orientation of the spin changes from down to up and the curve is acting ferromagnetically. At the critical temperature of 700 K, the order parameter is continuous, and there is a transition of second order from ferromagnetic state to paramagnetic state accompanied by broken symmetry.

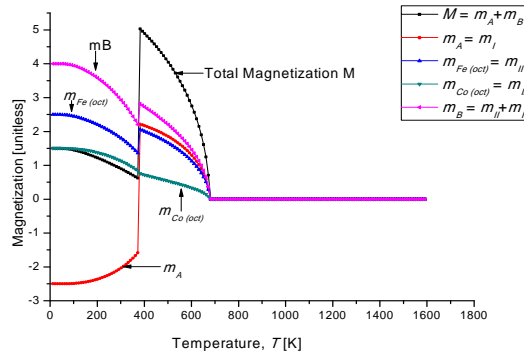


Figure 7: Total and partial magnetizations in the absence of crystal fields. The values of the exchange interaction constants are given in Table 2.

In the presence of the crystal field in the tetrahedral site of the iron (Figure 8), there is a magnetic frustration at the temperature of 500 K, corresponding to the transition of first order from the ferrimagnetic to ferromagnetic state. The order parameter is discontinuous at this temperature; above this temperature, the orientation of the spin changes from negative to positive to have a ferromagnetic

behavior. The order parameter is continuous, and it vanishes at the critical temperature of 1050 K. At this temperature, the transition of second order from ferromagnetic to paramagnetic is accompanied with broken symmetry, and then the system loses its magnetization to become 0.

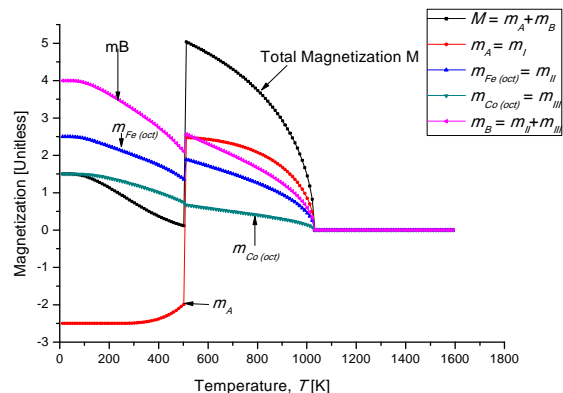


Figure 8: Total and partial magnetizations when crystal field of Fe tetrahedral site is 1160 K. The values of the exchange interaction constants are given in Table 2.

J_{AA}^{Fe-Fe}	J_{AB}^{Fe-Fe}	J_{AB}^{Fe-Co}	J_{BB}^{Fe-Co}	J_{BB}^{Fe-Fe}	J_{BB}^{Co-Co}
-14.0	-28.0	-22.7	-10.0	-9.0	+46.0

Table 2: Calculated ion-to-ion exchange interactions J for CoFe_2O_4 [15]

At low temperature (Figure 9), the system is acting as a ferrimagnetic state. The order parameter is different than 0 with increasing temperature. There is a transition of first order at the temperature of 430 K, and for Figure 10 at the temperature 480 K, the system changes from the ferrimagnetic to ferromagnetic state. By the effect of the crystal field of Fe octahedral site, the orientation of the spin changes from positive to negative and from up to down, and the magnetization becomes negative (Figure 10). This magnetization curve is called type N [16]. For Figure 9, the spin orientation changes from down to up, and the magnetization becomes positive. This magnetization curve is called type P [16], but all spins are oriented in the same direction which gives ferromagnetic behavior. At high temperature, there is a transition of second order at the Curie temperature of 700 K (Figure 9) and 930 K (Figure 10). There is broken symmetry accompanied from ferromagnetic state to paramagnetic state, where the order parameter is equal to zero. Above this temperature, the cobalt ferrite loses its magnetization.

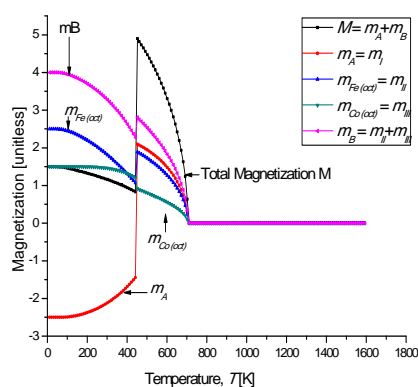


Figure 9: Total and partial magnetizations when crystal field of Co octahedral site is 928 K. The values of the exchange interaction constants are given in Table 2.

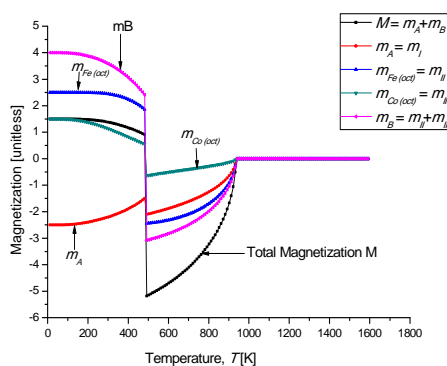


Figure 10: Total and partial magnetizations when crystal field of Fe octahedral site is 1160 K. The values of the exchange interaction constants are given in Table 2.

In the presence of the crystal fields for all sites, a first order transition occurs at low temperature and a second order transition at high temperature in Figure 11. Before the first transition, the partial magnetization of the two sublattice have different signs and have ferrimagnetic behavior. At the first transition, it is observed that the system changes from the ferrimagnetic to ferromagnetic state.

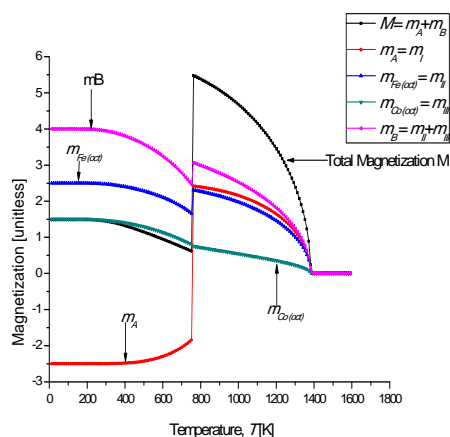


Figure 11: Total and partial magnetizations when crystal fields are present for all sites of 116 K. The values of the exchange interaction constants are given in Table 2.

4 Conclusions

Our investigations have revealed many interesting results. The magnetization depends on the exchange constants and crystal fields. A new magnetic behavior was observed for cobalt ferrite as magnetic frustration. A first order phase transition from ferrimagnetic to ferromagnetic phase was found at low temperature, and a second order transition from ferromagnetic to paramagnetic phase was observed at high temperature. Also, there was a second phase transition from ferrimagnetic state to paramagnetic state. The investigations also revealed that the phase transition temperatures depend on the crystal fields of the octahedral and tetrahedral sites. On the other hand, the magnetization curves shift to higher temperatures when the exchange interactions values are stronger.

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